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ABSORPTION OF SO₂ INTO LIME SLURRIES:
ABSORPTION RATES AND KINETICS

Edward Vivian

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ABSTRACT

The absorption of sulfur dioxide from sulfur dioxide-nitrogen gas mixture into water and lime solutions and slurries was studied in a short wetted wall column at approximately one atmosphere and 25 deg. C. The mole per cent of sulfur dioxide in the gas was varied from 0.03 to 0.37. In solutions of calcium hydroxide greater than 0.01 g.mole/liter and in slurries the system appeared to be gas absorption accompanied by an "infinitely" rapid irreversible second-order reaction in the liquid phase. The only effect of the solid in the slurries was to increase the absorption capacity. In water the system appeared to be gas absorption accompanied by a fast reversible hydrolysis reaction in the liquid phase. The major resistance to gas absorption at these concentration levels was found to be in the gas phase and at the lowest concentrations studied the system was gas phase controlled.

FOREWARD

The work reported here was carried out in accordance with Task Order No. 4 under HEW Contract CPA-68-02-0018. The principal investigator was J. Edward Vivian, Professor of Chemical Engineering. Research assistants who carried out the laboratory work were W. D. Franklin, R. N. Hindy and H. F. Jackson.

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SUMMARY

Restrictions on the emission to the atmosphere of sulfur dioxide have generated the need for effective methods for its removal from various waste gas streams such as stack gas from power plants burning sulfur-bearing fuels. One of the techniques under investigation is the absorption of the sulfur dioxide into lime slurries in water. This absorption system involves gas absorption accompanied by simultaneous chemical reactions in the liquid phase, and because of the low solubility of calcium hydroxide in water slurries are used in order to provide sufficient absorption capacity. This study was concerned with the effect of the reactions in the liquid phase upon the rate of absorption of sulfur dioxide by the slurries.

The experimental data were obtained with a short wetted wall column in which sulfur dioxide in nitrogen flowed counter to a falling film of liquid. Rates of absorption of sulfur dioxide into calcium hydroxide solutions and slurries and into water were measured at approximately 25 deg. C and one atmosphere total pressure. The concentration of sulfur dioxide in the gas was varied from 0.03 to 0.37 mole percent. Liquid phase absorption coefficients were obtained by deducting the gas phase resistance from the overall resistance derived from the experimental data. Comparison of these liquid phase coefficients with data on liquid phase controlled physical absorption permitted the calculation of the enhancement factor for the effect of liquid phase reactions on the absorption rate.

At the concentration levels used in this study the major part of the resistance to absorption both into slurries and into water was in the gas phase, and at the lowest concentrations the process was entirely gas phase controlled.

The absorption of sulfur dioxide into calcium hydroxide solution and

slurries appeared to be a system of gas absorption accompanied by an "infinitely" rapid second-order irreversible chemical reaction involving molecular (unhydrolysed) sulfur dioxide and hydroxide in solution. The rate of solution of solid calcium hydroxide did not appear to influence the absorption process at the interface. The effect of the solid in suspension was to increase the capacity of the liquid phase to absorb sulfur dioxide. This mechanism indicates the need in continuous contacting to provide hold-up to allow for the dissolution of the solid in the slurry to maintain the concentration of hydroxide near saturation.

The absorption of sulfur dioxide into water is a system of gas absorption accompanied by a fast reversible hydrolysis reaction. The reaction is sufficiently rapid to maintain hydrolysis equilibrium in the liquid as sulfur dioxide diffuses away from the interface. The enhancement factor for this case becomes very large at low concentrations of sulfur dioxide in the gas, and consequently, the system becomes gas phase controlled at these concentration levels. At calcium hydroxide concentrations greater than about 0.01 g.mole/liter the rate of absorption of sulfur dioxide into these hydroxide solutions was somewhat greater than that observed for the absorption into water under similar conditions.

Experimental work on the absorption of sulfur dioxide into slurries in a continuous absorber such as a long wetted wall column or a packed bed of spheres in which the liquid holdup undergoes repeated exposure to the gas followed by bulk mixing is needed to supplement these short wetted wall data to show the effect of the rate of dissolution of the solid on the absorption process.

INTRODUCTION

The absorption of sulfur dioxide into alkaline media is an important process which is receiving considerable attention as a prime means of controlling sulfur dioxide emission in stack gas from the combustion of sulfur-bearing fossil fuels. The process has been widely used in the process industries and in particular in chemical pulping, and the technology to meet the requirements of these industries is available. However, the scale of operations and particularly the concentration ranges of sulfur dioxide in feed gas and exhaust gas encountered in emission control problems impose new and more stringent requirements on this technology. For example, process exhaust gas may be the feed gas for emission control processes, and these processes are required to reduce sulfur dioxide levels to a few hundred parts per million.

The absorption of sulfur dioxide from gaseous mixture into alkaline media is a process involving gas absorption accompanied by simultaneous chemical reactions in the liquid phase. Depending on the relative rates of diffusion and reaction one or the other phenomenon may be the controlling factor. An understanding of the interaction of diffusion and reaction is necessary for design of equipment and also for operation of such processes since operating conditions may affect the relative rates significantly. Fundamental kinetic data are often not available, and furthermore since such reactions fall in the category of "fast reactions" fundamental kinetic data are difficult to obtain independently without the complicating factors involved in the combined diffusion and reaction processes. Consequently these kinetic data are generally determined in the laboratory by comparing absorption rates with and without reaction under carefully controlled fluid dynamic conditions. Laminar jets and short wetted wall columns have been

useful for this work.

Several alkaline reactants can be used to absorb sulfur dioxide. Sodium hydroxide, sodium carbonate, sodium sulfite and magnesium hydroxide are effective reactants of commercial importance for emission control, providing the process includes a chemical regeneration system. The only reactants for sulfur dioxide absorption which appear to be economically justifiable in a once-through process are calcium hydroxide and calcium carbonate. Since plant investment and technological development will be considerably less for chemical processing which does not include recovery operations, substantial emphasis is being directed to the development of lime/limestone absorbers for first generation plants for sulfur dioxide emission control. In view of the low solubility in water of these reactants aqueous slurries must be used to provide adequate absorption capacity. Thus in developing an absorption model for absorption of sulfur dioxide into these slurries not only is consideration of diffusion and reaction in the liquid phase important but also the rate of dissolution of the solid reactant.

In this investigation an attempt was made to determine the effect of the liquid phase reactions of sulfur dioxide with lime slurries upon the rate of absorption of sulfur dioxide under known fluid dynamic and diffusion conditions with a view to determining the rate limiting steps. A short wetted wall column was used and the laboratory work was limited to reagent chemicals and to concentrations of sulfur dioxide in the gas phase of interest in the emission control program.

THEORETICAL CONSIDERATIONS

Sulfur dioxide dissolves in water and undergoes hydrolysis to form a solution of molecular unhydrolysed SO_2 and hydrogen, bisulfite and sulfite ions. Sulfurous acid (H_2SO_3) is believed not to exist in significant amount. Equilibrium exists between the various species in solution and between the unhydrolysed molecular SO_2 and the partial pressure of SO_2 in the gas phase. The equilibrium between SO_2 in the gas and the unhydrolysed molecular SO_2 follows Henry's law and can be written in the form:

$$C_A = Hp$$

where C_A is the unhydrolysed molecular SO_2 concentration, g.mole/liter, and p is the partial pressure in atmospheres in the gas phase. The equilibrium established in the liquid phase for the hydrolysis of the dissolved SO_2 to form bisulfite can be written in the form:

$$K_1 = \frac{[\text{HSO}_3^-][\text{H}^+]}{C_A}$$

The dissociation of HSO_3^- is very small unless the hydrogen ion concentration is suppressed by the presence of alkali. Consequently the total concentration C_T of sulfur dioxide in solution can be represented by the sum of the concentrations of the unhydrolysed molecular SO_2 , C_A , and the bisulfite ions, C_E :

$$C_T = C_A + C_E$$

Combining this with the expression for Henry's law to substitute for the molecular SO_2 concentration and the expression for the dissociation constant to substitute for the bisulfite concentration and noting that the concentration of hydrogen and bisulfite ion concentrations are essentially equal an expression for the gas-liquid equilibrium for sulfur dioxide in

water is obtained:

$$C_T = H p + \sqrt{K_1 H p}$$

The importance of this expression lies in the fact that it permits the evaluation of the Henry's law constant. This constant is required to predict the interfacial concentration of unhydrolysed molecular SO_2 in an absorption process.

Several investigators have studied the equilibrium solubility of sulfur dioxide in water. The work of Johnston and Leppla (3) is representative of these studies and has been used in this work to derive the Henry's law constant. The data are shown in Figure 1 where $C_T/\sqrt{p}$ has been plotted against $\sqrt{p}$ so that the slope of the isotherm is equal to the Henry's law constant, H , and the intercept is equal to $\sqrt{K_1 H}$. The constants are given as a function of temperature in Figure 2. Equations for these functions are:

$$\ln H = \frac{3175.2}{T} - 10.4523$$

$$\ln K = \frac{2362.6}{T} - 11.929$$

where H is given in g.moles/liter-atm, K_1 in g.moles/liter and T in degrees Kelvin. It is to be noted that the values of K_1 derived from these gas-liquid equilibrium data agree closely with values reported in the literature.

The model assumed in this investigation for the absorption of sulfur dioxide into water is based on diffusion of SO_2 from the bulk of the gas phase at a partial pressure p across a gas phase resistance to the gas-liquid interface where the partial pressure p_i establishes an equilibrium concentration C_{Ai} of unhydrolysed molecular SO_2 in the liquid interface. Molecular SO_2 is removed from the interface by diffusion as molecular SO_2 and by reaction with water. Depending on the relative rates of diffusion and reaction, liquid phase equilibrium between the species in solution at

FIGURE 1

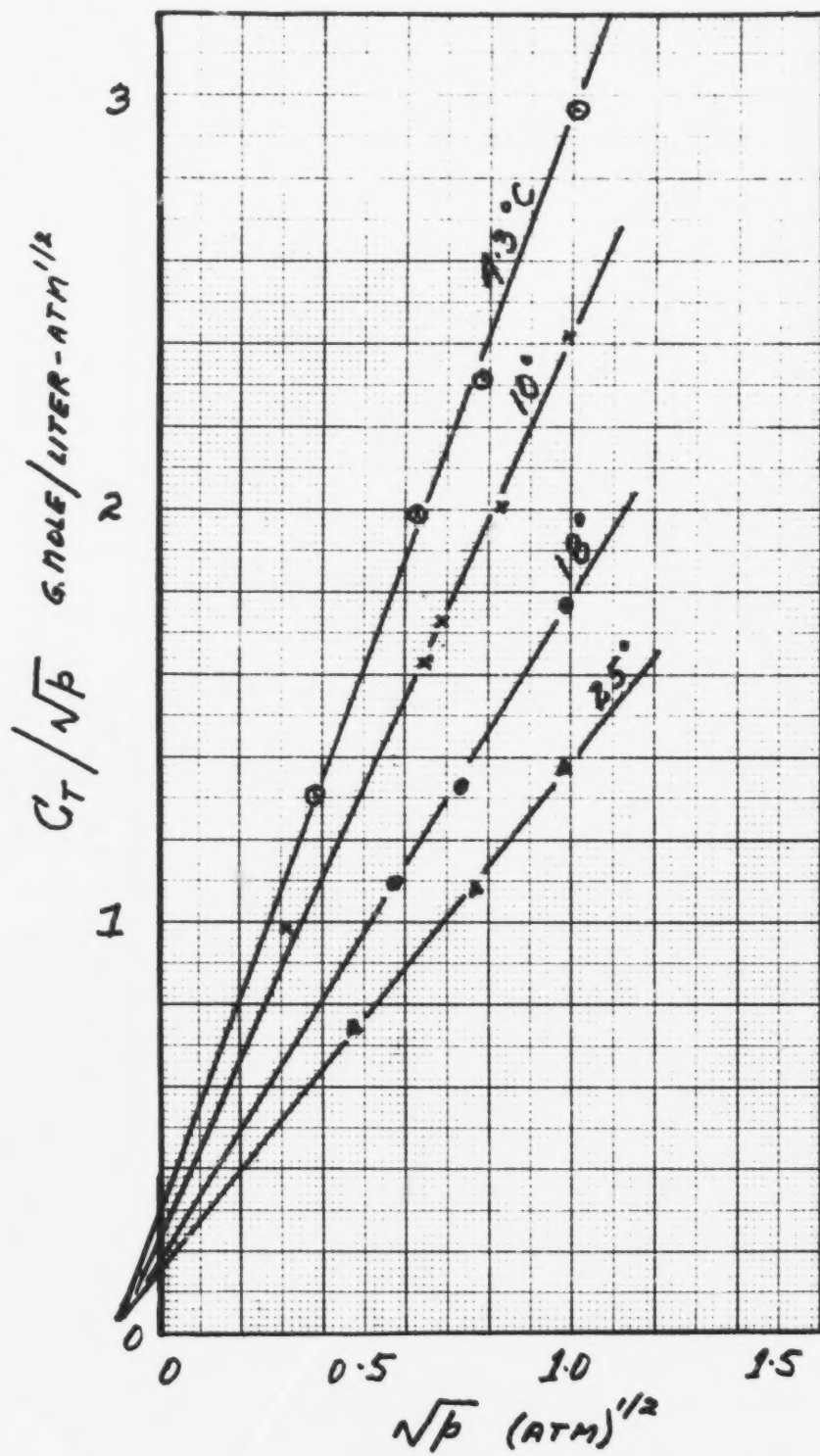
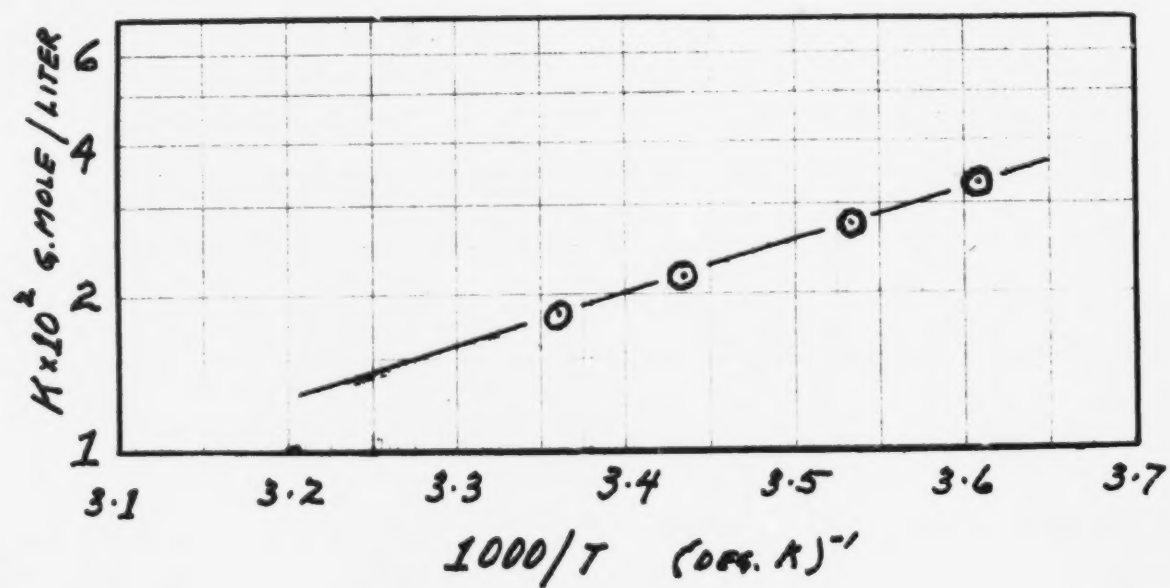
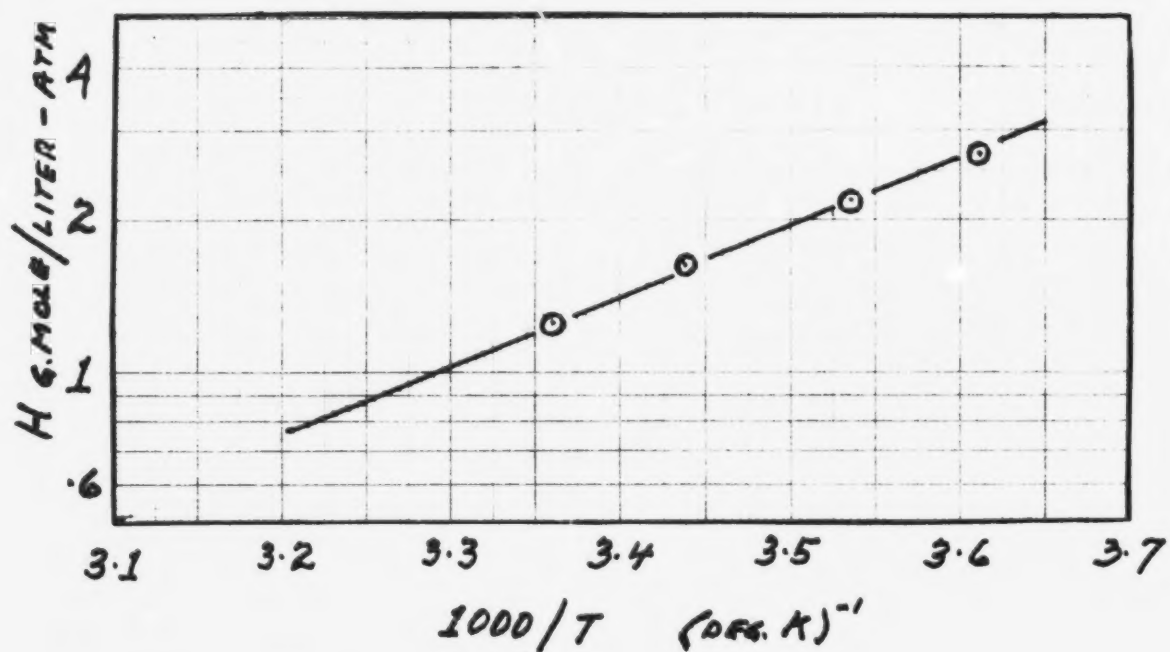


FIGURE 2



any given distance from the interface may or may not be maintained.

Eigen, Kustin and Maass (1) report data on the hydrolysis reaction:



which indicate the forward rate as written to have a pseudo-first order rate constant in excess of 10^6 sec^{-1} . Relative to ordinary diffusion rates this is a very fast reaction, and it is expected that the various species will be approximately in equilibrium during diffusion away from the interface.

In cases involving absorption with simultaneous chemical reaction it has been convenient to retain the usual forms of the absorption rate equation and to allow for the effects of the associated chemical reactions by an enhancement factor. Thus the rate equation becomes:

$$N_A = \phi k_L^* (C_{A_i} - C_A)$$

where N_A is the solute flux (g.moles/sec-cm^2) and k_L^* is the physical absorption coefficient dependent on physical properties and fluid dynamics of the system. The driving-force ($C_{A_i} - C_A$) is the difference between the concentration at the interface and in the bulk liquid of the specie entering the liquid phase, in this case unhydrolysed molecular SO_2 , and ϕ is the enhancement factor dependent on the relative rates of diffusion and reaction. For a limited number of absorption models ϕ can be estimated from properties of the system.

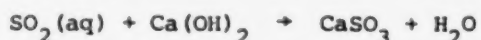
Applying the concept of equilibrium among all species during the diffusion of SO_2 away from the interface in the absorption of SO_2 into water the enhancement factor was found to be:

$$\phi = 1 + \frac{D_E}{D_A} \sqrt{\frac{K_1}{C_{A_i}}} \left(\frac{1}{1 + \sqrt{C_A/C_{A_i}}} \right)$$

where D_A and D_E are the diffusivities of molecular SO_2 and bisulfite ion

respectively, and K_1 is the equilibrium constant for the reaction of SO_2 with water. The model used here to derive this expression for ϕ was based on film theory. The corresponding expression for penetration theory was not available, but the two theories are not expected to differ significantly in this case.

To model the absorption of SO_2 into lime slurry the reaction of SO_2 with hydroxyl ion and the dissolution of the lime particles must be included. At very low concentrations hydroxyl ions will have negligible effect on increasing the rate of absorption over the rate into water. However, as the hydroxyl ion concentration is increased eventually the rate of absorption will be governed by the reaction of SO_2 with hydroxyl ion to produce bisulfite and sulfite ions. These reactions are expected to be very rapid. For the case where there is no sulfite in the initial absorbent liquid, hydroxide will diffuse from the bulk toward the interface as SO_2 in one or more forms diffuses away from the interface. This is a situation typical of a fast irreversible (homogeneous) second-order reaction in the liquid phase. The overall effect is:



The fact that CaSO_3 has very limited solubility and will precipitate will have only a secondary effect on the rate at which $\text{SO}_2(\text{aq})$ is removed from the interface. The presence of solid $\text{Ca}(\text{OH})_2$ in the slurry however may affect the rate depending on its rate of dissolution.

If the rate of dissolution is relatively slow, the absorption process during a single exposure will be similar to the infinitely rapid irreversible reaction case involving reacting species in solution. The ϕ -values which will lie on the asymptotes on the Peaceman-van Krevelen plot are independent of kinetic rates and of liquid flow rate or exposure time and are approximately given by:

$$\phi = 1 + \frac{C_B}{C_{A1}} \sqrt{\frac{D_B}{D_A}}$$

where C_B is the saturated calcium hydroxide concentration in the bulk liquid.

On the other hand if the rate of dissolution of the calcium hydroxide particles is sufficiently rapid relative to the rate at which hydroxide in solution is consumed by the absorbed SO_2 so that a concentration of hydroxide close to saturation is maintained, the reaction accompanying the absorption will appear to be pseudo-first order. The ϕ -values will lie along the 45 degree line on the Peacemen-van Krevelen plot, or in other words the ϕk_L^* product will be a constant independent of flow rate and equal to $\sqrt{k D_A C_B}$ where k is the second-order reaction rate constant.

Thus experiments measuring the rate of absorption of SO_2 into lime slurries at different flow rates (which varies k_L^*) should give an indication of whether the rate of dissolution of the solid is rapid enough to increase the overall rate of absorption above that expected for absorption into the homogeneous liquid phase or whether the advantage in the presence of the solid is only to increase the capacity of the liquid phase to dissolve and react with SO_2 . In the latter case, holding time between surface exposures to complete reaction and saturate the liquid will be required to use the slurry reactant effectively.

Since sulfur dioxide has appreciable solubility in water and undergoes rapid reactions in the liquid phase, there will be significant gas phase resistance to absorption. To reduce the data on SO_2 absorption to obtain data on liquid phase phenomena an estimate of the gas phase resistance must be made and deducted from the overall resistance. The short wetted wall column was used to study gas phase controlled absorption by Behrmann (8) and by Schoenburg (9). Liquid flow rate had negligible effect on the gas phase coefficient, and the results for the gas phase were correlated by reporting the Sherwood number, N_{Sh} , as a function of

the Schmidt number, N_{Sc} , and Reynolds number, N_{Re} as shown in Figure 3. These data were used to estimate the gas phase resistance in this work. Additivity of resistances as demonstrated by Mayr (2,4) was assumed in computing the liquid phase resistance. Thus the additivity equation appropriate for this work can be written:

$$\frac{1}{(K_c)_G} = \frac{1}{(k_c)_G} + \frac{P_G}{HP \phi k_L^*}$$

where $(K_c)_G$ and $(k_c)_G$ are the overall and individual gas phase coefficients, k_L^* is the liquid phase physical absorption coefficient, P and P_G are the total gas pressure and molal gas density and H is Henry's law constant. It should be noted that as ϕ increases the controlling resistance will shift to the gas phase, and at low liquid phase resistance calculation of the small difference between the overall and the individual gas phase resistance will be subject to difficulties due to precision of measurements.

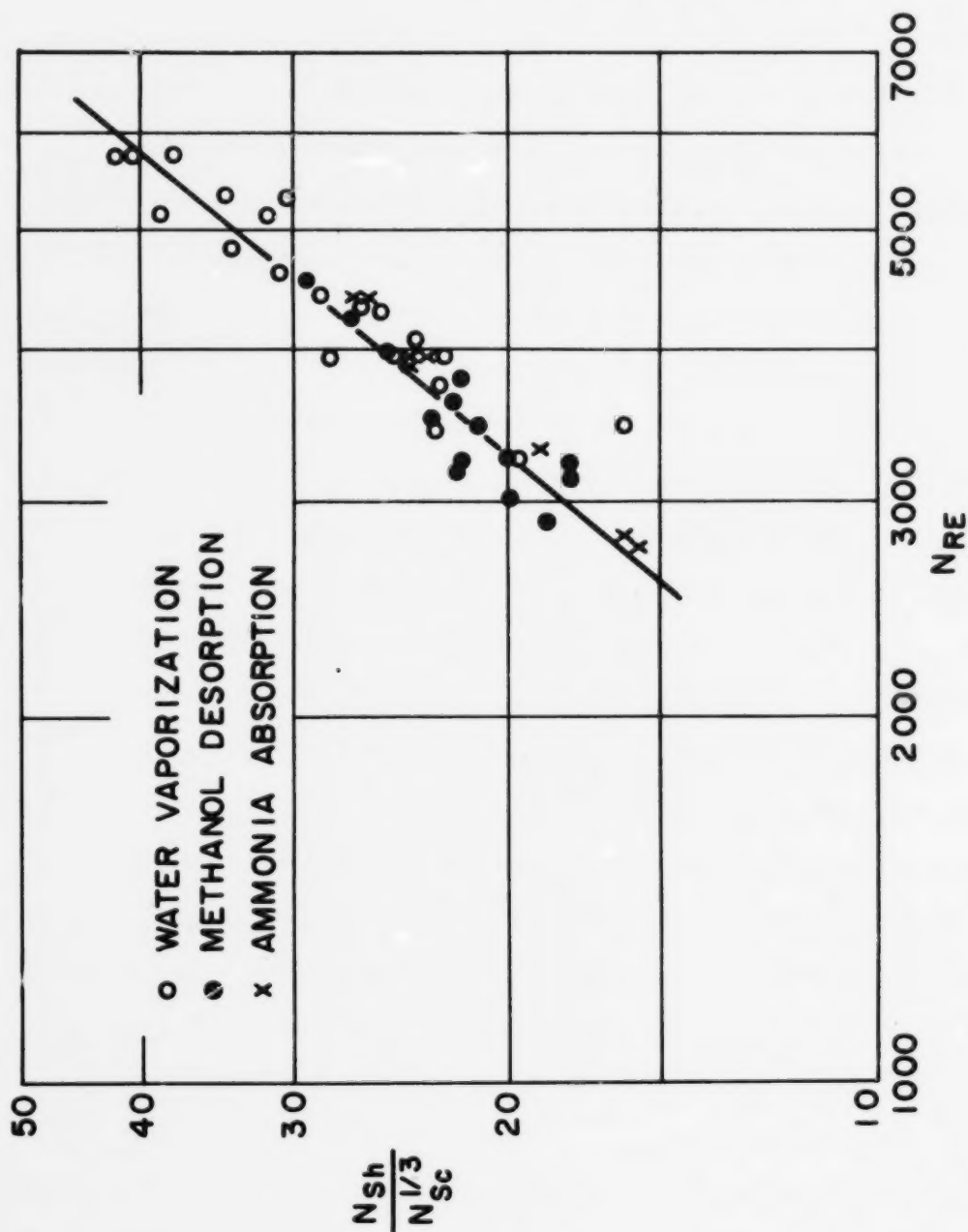


FIGURE 3

APPARATUS AND PROCEDURE

In the study of the relatively rapid processes at the gas-liquid interface which occur in gas absorption the development of suitable experimental techniques to obtain reproducible data under known experimental conditions was an important problem. Several laboratory devices have been used with varying success each with its particular advantages and disadvantages.

Two of these devices, the laminar jet developed by Pigford and Scriven and the short wetted wall column developed by Vivian and Peaceman perform closely according to theoretical predictions. The laminar jet gives highly reproducible data and is relatively easy to operate. However, it is limited to the use of a pure gas phase (i.e., no gas phase resistance), and therefore, it could not be applied for this study involving absorption of SO_2 at very low partial pressures.

The short wetted wall column has been used to study both liquid and gas phase controlled absorption. It provides surface exposures of the same order of magnitude as many commercial types of absorbers, and penetration theory can be used to analyse data obtained with it. As originally designed, it was not suitable to operate with a slurry system. However, a special feed system was designed and constructed which allowed its operation with slurries, and all the data reported here were obtained with a short wetted wall column.

Operating a relatively small flow system with slurries presents considerable difficulty, and in this case particularly with maintenance of uniform slurry concentration at the column. By use of a circulating system with a short downward-sloping drawn-off through a small-bore flow meter directly to the head of the short wetted wall column data with

a fair degree of reproducibility could be obtained.

The overall apparatus is shown schematically in Figure 4. Slurry was prepared by mixing distilled water and reagent grade calcium hydroxide in the feed tank in which an agitator maintained the hydroxide in suspension. A pump circulated the slurry through a small diameter line at high velocity to an open surge tank mounted above the column. From the surge tank the slurry flowed directly back to the feed tank. Flow of slurry to the column was drawn from the line to the surge tank through the calibrated small-bore flow meter. Slurry discharged from the column was discharged to waste except when liquid samples were being collected. Liquid samples were collected under N_2 to reduce possible oxidation of SO_2 .

The gas phase was prepared by mixing in a baffled section of the gas line metered flows of N_2 and SO_2 supplied by cylinders. The N_2 flow meter was calibrated by use of a calibrated dry test meter and the SO_2 flow meter was calibrated by analysis of the mixed gas streams. Essentially all of the data were taken at a Reynolds number of about 3000. This was chosen as a balance between the need to minimize gas phase resistance and the need to maintain an undisturbed liquid layer on the column wall.

The short wetted wall column is shown in outline in Figure 5, and is the same construction as described elsewhere (8).

A special head for the column was constructed to avoid dead spots where slurry solids could collect and to give a uniform liquid layer on the wall. After considerable experimentation the design shown in Figure 6 was developed. All of the data reported here were obtained with the use of this head.

Run procedure consisted of continuous operation of the flow systems to achieve steady-state after which the liquid phase to and from the column was sampled and pertinent data on operating conditions were read. Only

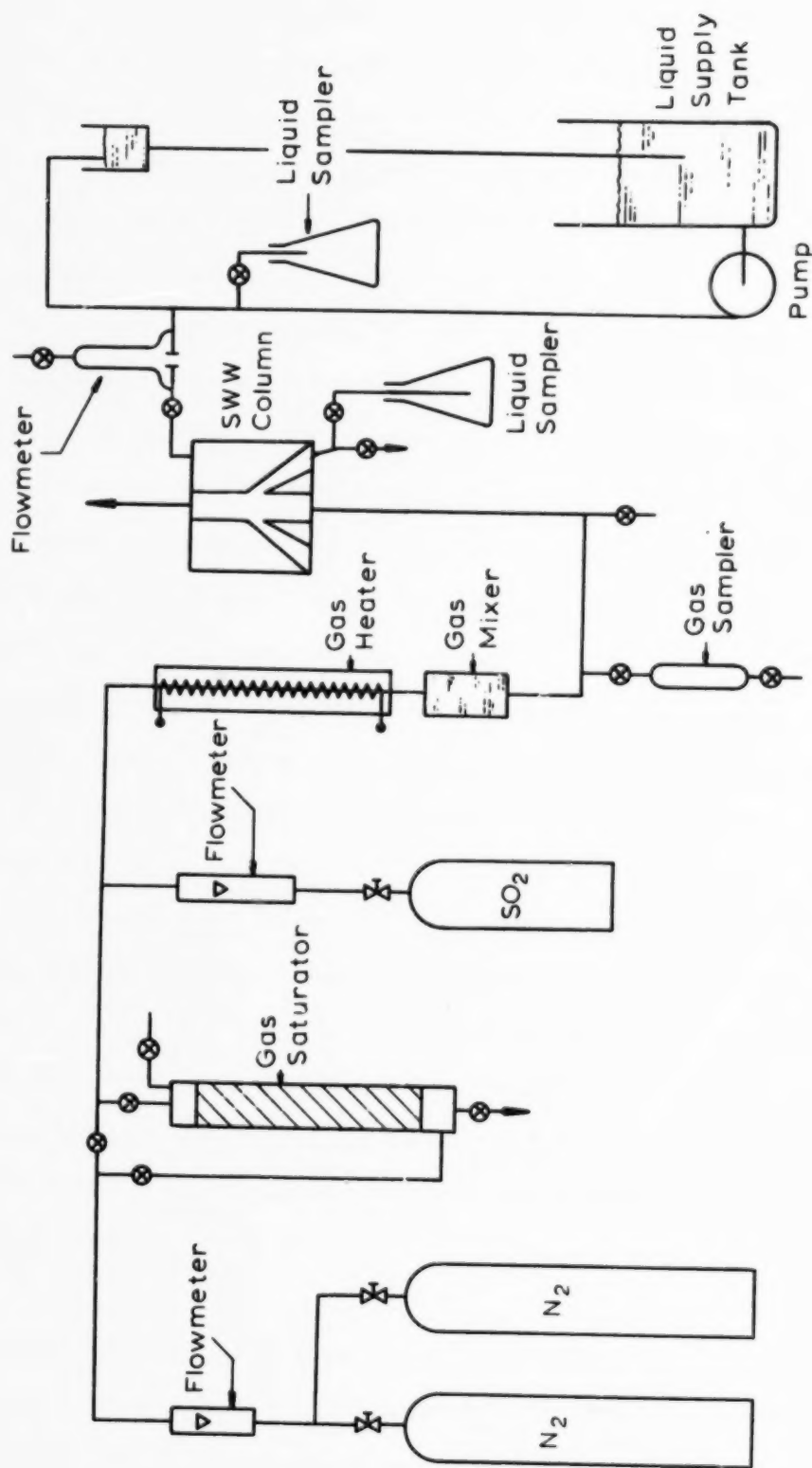
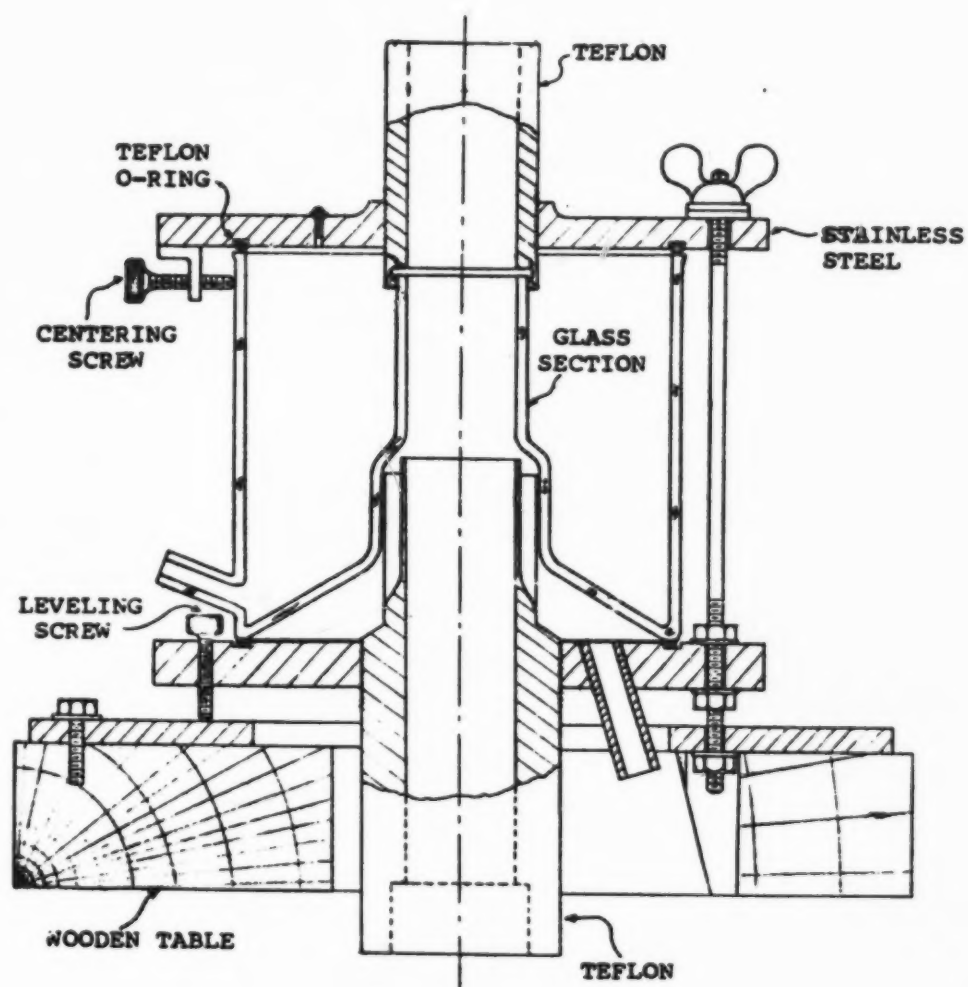


FIGURE 4
SCHEMATIC DIAGRAM OF APPARATUS
ABSORPTION OF SO_2 IN SLURRIES IN SHORT WETTED WALL COLUMN

FIGURE 5

SHORT WETTED WALL COLUMN ASSEMBLY

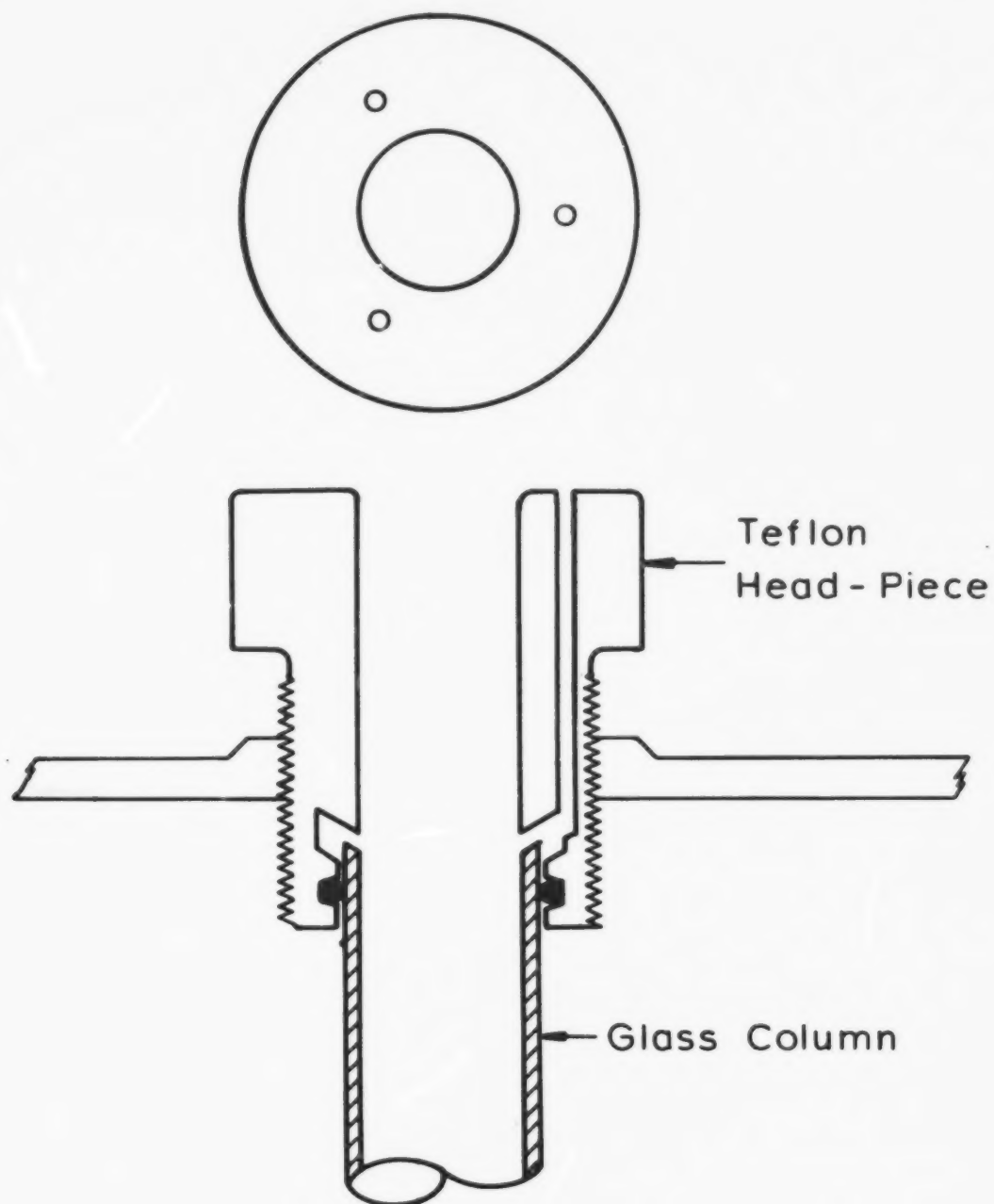


FIGURE 6

the outlet liquid analyses have been reported here since, in general, the total alkali content of both samples agreed within operating precision.

The procedure used in runs with calcium hydroxide solutions and with water was essentially the same.

In spite of the high velocity circulating liquid system and short draw off to the column, entirely satisfactory operation with a calcium carbonate slurry was not obtained before the laboratory work was terminated. Further modification of the liquid feed system would have been required to obtain satisfactory data.

Details of the analytical methods and equipment calibration are given in Appendix A.

RESULTS AND DISCUSSION

The rate of absorption of SO_2 into lime slurry was calculated from the volumetric flow rate of the slurry and the concentration of total SO_2 (i.e., unhydrolysed SO_2 , bisulfite and sulfite ion) in the slurry leaving the short wetted wall column. An overall coefficient, $(K_c)_G$ expressed as cm/sec, was obtained by dividing the rate of absorption by the interfacial area of the column, the molal density of the gas and the mole fraction of SO_2 in the entering gas. The data are summarized in Appendix C. In order to interpret these data it was necessary to distinguish between the components of the overall resistance to absorption.

The gas phase resistance was estimated from previous work on the short wetted wall column (8,9), and assuming additivity of resistances as demonstrated by Mayr (2,4) the liquid phase resistance was calculated by deducting the gas phase resistance from the overall resistance. This liquid phase resistance was assumed to be the result of kinetic and diffusional effects, and the liquid phase coefficient is reported in Appendix C as the product ϕk_L^* where k_L^* is the absorption coefficient without chemical reaction and ϕ is the enhancement factor to account for the effect of chemical reaction in the liquid phase. The dependence of the absorption coefficient without chemical reaction, k_L^* , on liquid rate and fluid properties is well understood, and by estimating k_L^* from previous work on the short wetted wall column such as that of Mayr (4) the value of ϕ was obtained.

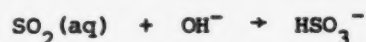
It should be noted that for the absorption conditions encountered in this work, the liquid phase resistance accounted for only a small fraction of the total resistance with the result that ordinary precision of measurements introduced considerable uncertainty in the small differences

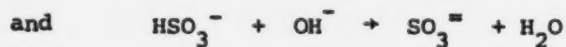
representing the liquid phase resistances. This uncertainty directly affected the calculated values of the enhancement factor. Consequently the value of these data lie not in their absolute value but in their order of magnitude and directional trends in supporting theoretical considerations. In the runs with the lowest SO_2 concentration the calculation of a liquid phase resistance had no significance within the precision of the experimental data, and consequently, no conclusion can be drawn from those runs except that in fact the absorption process becomes gas phase controlled as the concentration of SO_2 in the gas decreases.

The absorption of SO_2 into lime slurries and solutions appears to be a case of absorption accompanied by very fast chemical reactions. Furthermore in the presence of excess hydroxyl ion the reactions appear irreversible. Theory indicates that under these conditions an approximation for the enhancement factor is given by:

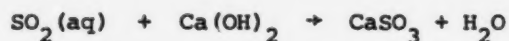
$$\phi = 1 + \left(\frac{C_B}{\nu C_{A_i}} \right) \sqrt{\frac{D_B}{D_A}}$$

where C_B is the concentration of reactant B in the bulk of the liquid, C_{A_i} is the concentration of solute A in the liquid at the interface and ν is a stoichiometric factor giving the number of molecules of B which react with A. D_A and D_B are the respective diffusivities. In the system under study here, C_B is the calcium hydroxide in solution and C_{A_i} is the molecular SO_2 in solution at the interface. C_{A_i} is assumed to be in equilibrium with the gas phase concentration at the interface. The stoichiometric factor is 1, assuming that the reactions of importance in the presence of relatively high hydroxyl ion concentration are:





which can be written as an overall reaction to indicate the relative quantities of diffusing species:



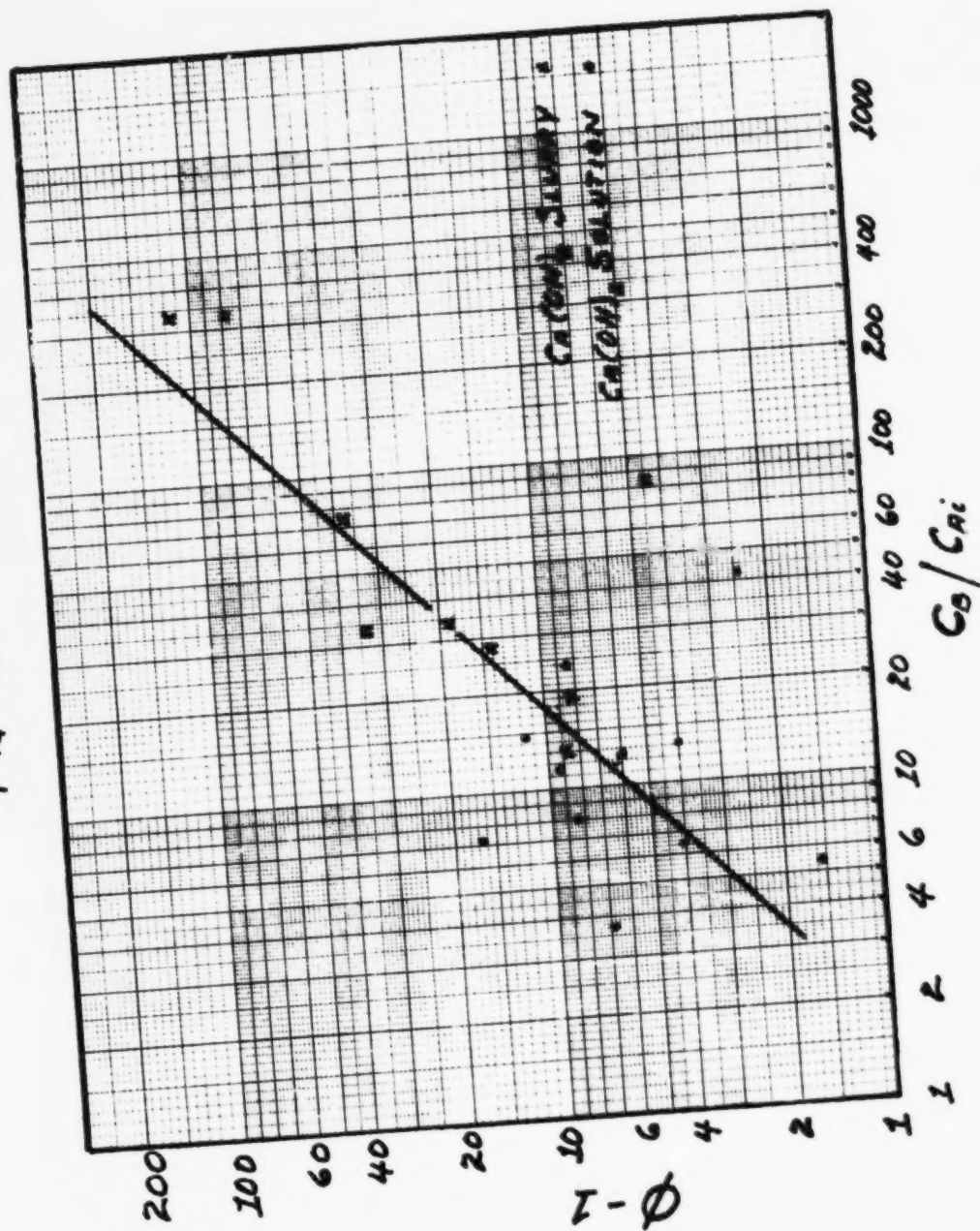
The data obtained for the absorption into lime slurries and solutions are plotted in Figure 7 to show the relationship of $\phi-1$ to the ratio C_B/C_{A_i} . In the runs with the slurries C_B was assumed to be saturation at the liquid temperature. The line through the data is drawn with a slope of 1 as suggested by theory. While the data are somewhat scattered due to difficulties with precision of data they tend to substantiate the assumption for these conditions of absorption accompanied by very rapid second-order irreversible chemical reaction.

The ratio C_B/C_{A_i} is based only on a small range of C_B from half saturation to saturation. The value of C_{A_i} however, varies widely due to changes in gas phase concentration and gas phase driving force. The CaSO_3 formed had very low solubility and precipitated. In the runs with clear $\text{Ca}(\text{OH})_2$ solutions this precipitate was readily visible in the column.

These experiments indicate that the presence of solid calcium hydroxide had little effect on the absorption rate which depended only on the calcium hydroxide concentration in solution and not on slurry concentration. Even though a highly reactive analytical grade of calcium hydroxide was used to prepare the slurries, no effect of solid concentration is evident. Apparently the rate of solution of the solid was not sufficiently rapid to influence the processes occurring at the interface during the 0.1 sec (approx) exposure time.

These rate measurements were made for a single exposure of the surface of the liquid layer, initially of uniform equilibrium composition. Repeated exposure would, of course, deplete the reactant in solution

FIGURE 7



unless it were replenished by dissolution of the solid in the slurry. Thus the rate of dissolution of the solid assumed importance in maintaining the capacity of the liquid to absorb SO_2 rather than participating in reactions at or near the interface. In view of this mechanism it should be possible to rank the behavior of various lime slurries by observing their rates of solution in simple liquid phase measurements without the necessity of characterizing them in actual absorption measurements which are difficult to make. The mechanism also indicates the desirability of providing adequate liquid holdup per unit interfacial area to allow dissolution of solid and re-saturation of the liquid phase between surface exposures. To perform satisfactorily, the rate of dissolution per unit volume of slurry multiplied by the volume of holdup per unit interfacial area must be equal to or greater than the rate of absorption per unit interfacial area.

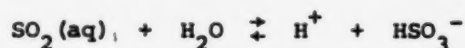
The short wetted wall column is well suited for investigating absorption phenomena which occur at or near the interface and which conform approximately to the surface renewal or penetration theory model of gas absorption. Exposure times are relatively short, ranging from about 0.05 to 0.2 seconds. Penetration depths are relatively small compared to the thickness of the liquid layer. Consequently bulk phenomena cannot interact to any great extent with what occurs in the liquid at the interface until mixing occurs following the surface exposure.

In the system of interest here the absorbed SO_2 reacted with hydroxide in solution near the interface and depleted the hydroxide concentration in that region. Solution of solid hydroxide proceeded in the bulk liquid after mixing with the depleted surface liquid. To observe the overall effect of interfacial and bulk processes an experimental system which provides for repeated surface exposure and associated bulk

reaction volume is required in addition to the short wetted wall column. For example, rate data obtained with turbulent slurry film flow in a long wetted wall column or with slurry flow over a packed bed of spheres would probably be more representative of the overall process of absorption into calcium hydroxide slurry than the data obtained with the short wetted wall, and such data combined with the fundamental homogeneous rate data obtained with the short wetted wall column would allow analysis of the effect of the processes in the bulk liquid on the absorption rate.

Data were obtained for the absorption of SO_2 into water in the short wetted wall column over the same concentration range as used in the lime slurry studies. These data were taken to indicate the performance of the column and establish the experimental procedure without the complicating factors due to the calcium hydroxide. In addition they provide an indication of the effect of hydrolysis of SO_2 in water on the rate of absorption.

The rate of the hydrolysis of SO_2 in water has been studied (1,6), and the data obtained indicate only that it is a very fast reaction. The reaction is:



The few qualitative data available give rates so high that the maintenance of equilibrium in water during diffusion of SO_2 away from the interface would be expected. On this assumption mass balances on the rate of removal of various forms of SO_2 from the interface into the bulk of the liquid allow the calculation of the enhancement of the absorption rate due to the hydrolysis reaction. The absorption rate can be written as:

$$N_A = \phi k_L^* (C_{A1} - C_A)$$

where, as before, C_{A1} , C_A is the unhydrolysed molecular SO_2 in solution.

The effect of the hydrolysis reaction was shown to be:

$$\phi = 1 + \left(\frac{D_E}{D_A} \right) \left(\sqrt{\frac{K_1}{C_{A1}}} \right) \left(\frac{1}{1 + \sqrt{C_A/C_{A1}}} \right)$$

where K_1 is the equilibrium constant for the hydrolysis reaction, and D_A and D_B are the diffusivities of unhydrolysed and hydrolysed SO_2 respectively.

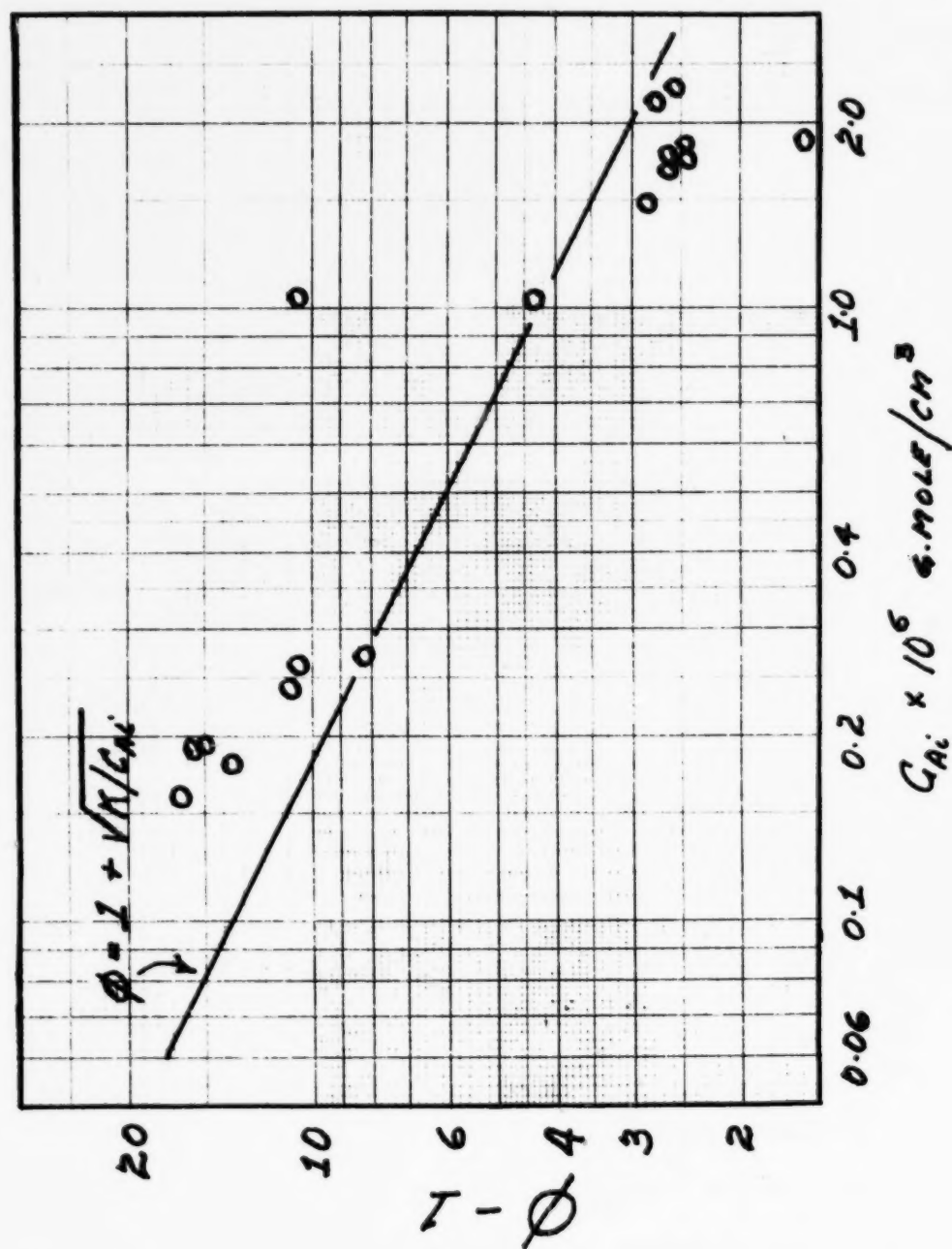
When the diffusivities of species A and B are nearly equal as in the SO_2 -water system (5), and the concentration of SO_2 in the bulk, C_A , is negligible relative to the concentration at the interface C_{A1} , the expression for the enhancement factor reduces to:

$$\phi = 1 + \sqrt{K_1/C_{A1}}$$

The data for the absorption of SO_2 into water are plotted in Figure 8 to show the relationship of $\phi-1$ to $\sqrt{K_1/C_{A1}}$. The line as indicated represents the theoretically derived relation for an assumed infinitely rapid hydrolysis reaction. Although the data are somewhat scattered due to the effect of precision of measurements in deriving the liquid phase resistance, the trend of the data substantiates the theory based on a very rapid hydrolysis reaction.

It is instructive to compare the hydrolysis reaction of SO_2 and water with that of Cl_2 and water. The two systems have many similarities, and the Cl_2 system has been extensively studied. Both solutes react directly with water to form hydrolysis products and establish a reaction equilibrium. The evidence seems to indicate that dissolved SO_2 reacts directly with water to form an essentially completely dissociated product consisting of hydrogen and bisulfite ions. Dissolved Cl_2 reacts directly with water to form hypochlorous acid and hydrogen and chloride ions. The rate of the

FIGURE 8



chlorine hydrolysis has been measured by at least three techniques which agree surprisingly closely. The rate is rapid but not as rapid as SO_2 hydrolysis appears to be.

The presence of hydrogen ions inhibits the hydrolysis of both Cl_2 and SO_2 . Under such conditions, absorption follows the laws of physical absorption, and the driving-force for mass transfer is the unhydrolysed molecular solute. At low hydrogen and hydroxyl ion concentrations data on the absorption of Cl_2 follow a pseudo-first order rate equation. At hydroxyl ion concentrations above 0.01 N Cl_2 hydrolysis involves hydroxyl ions and appears to be second-order and irreversible. It is likely that SO_2 follows a similar pattern in its reactions with water and alkali solutions, although apparently the hydrolysis reaction at medium and low pH appears to be very much more rapid than is the case with Cl_2 .

At high concentrations of SO_2 in the gas and liquid the reaction appears reversible and the rates of absorption approach physical absorption. As the concentration of SO_2 in solution and in the gas is decreased, the enhancement factor increases as the interfacial concentration C_{A_i} decreases with the result that at very low concentrations the absorption process will become controlled entirely by the gas phase resistance even for absorption into water.

A number of SO_2 -water runs (No. 52-57) were made with very low SO_2 flow rates (the lowest used in these experiments), and it is suspected that the flow meter did not operate reliably at this end of the scale. Considerable difficulty was experienced in this range during the calibration runs. It is not known whether this was due to the float sticking or to analytical procedures. However, the absorption data indicated that the SO_2 concentration in the gas calculated from the flow rates is too low since the overall gas phase coefficient cannot be greater than the individual gas phase co-

efficient. If it is assumed that the liquid phase offered negligible resistance in runs 52-57 so that the overall $(K_c)_G$ would be equal to $(k_c)_G$, the flowrates of SO_2 would be approximately 1.5 times the rates indicated in these runs. This appears to be within the precision of the calibration in this range of the flowmeter. Consequently these data serve only to substantiate the prediction that SO_2 absorption at very dilute gas concentrations becomes essentially gas phase controlled.

A few runs were made using a CaCO_3 slurry. These are reported in Table 3, Appendix C. Great difficulty was encountered in maintaining a stable slurry flow due to the settling and plugging characteristics of the CaCO_3 particles. Unfortunately, time did not permit resolution of these operating problems. Definitive conclusions cannot be drawn from this phase of the work.

Comparison of the magnitude of the enhancement factors for absorption into water and into alkaline solution reveals that for the lower hydroxyl concentration range (below 0.01 g.mole per liter) the enhancement is about the same as for water. Further work is required to indicate the actual effect of hydroxyl ion concentration, although these data indicate that above 0.01 g.mole $\text{Ca}(\text{OH})_2$ per liter the enhancement is expected to increase with alkaline concentration. In this behavior, SO_2 absorption into water and alkaline solutions appears to be similar to the Cl_2 -water system.

CONCLUSIONS AND RECOMMENDATIONS

The distribution of resistance to the absorption of SO_2 into lime slurry in the short wetted wall column depended on the gas phase concentration. At low concentrations (0.3 mole per cent SO_2) the major resistance was found to be in the gas phase, and at concentrations below 0.1 mole per cent the absorption process was essentially gas phase controlled.

The absorption of SO_2 into lime slurry appeared to be a system of gas absorption accompanied by an "infinitely" rapid second-order irreversible chemical reaction involving unhydrolysed molecular SO_2 and hydroxide in solution. The rate of solution of solid calcium hydroxide did not influence the absorption process at the interface during the short exposure time characteristic of the short wetted wall column. The effect of the solid calcium hydroxide was to increase the capacity of the liquid phase to absorb SO_2 . Adequate holdup of liquid would be required in a continuous absorber to allow sufficient dissolution of calcium hydroxide to maintain the hydroxide in solution near saturation.

The absorption of SO_2 into water is a system of gas absorption accompanied by a fast reversible hydrolysis reaction. The reaction is sufficiently rapid to maintain hydrolysis equilibrium in the liquid as SO_2 diffuses away from the interface. In agreement with theory the enhancement factor varied approximately inversely with the square root of the gas phase interfacial concentration, and the system became gas phase controlled at concentrations of SO_2 in the gas phase below 0.1 mole per cent.

The rates of absorption of SO_2 into water and into calcium hydroxide solutions of about 0.01 g.mole per liter were about the same, and the rate into hydroxide solutions increased slightly with increase in hydroxide concentration in solution.

Significant data on the absorption of SO_2 into calcium carbonate slurries could not be obtained with the equipment available.

Experimental work on the absorption of SO_2 in slurries in a long column or packed bed is needed in addition to studies on equipment such as the short wetted wall column in order to investigate the overall effect of interfacial and bulk liquid reactions since the dissolution process does not appear to affect the processes in the region of the interface.

APPENDIX

APPENDIX A
DETAILS OF PROCEDURE

1. Gas Flow Rate and Composition

The nitrogen-sulfur dioxide gas mixture feed to the column was prepared by mixing metered streams of nitrogen and sulfur dioxide. The rotameter used to meter the nitrogen gas from the supply cylinder was calibrated on air using a calibrated gas test meter. The small correction for variable conditions and from air to nitrogen was made as shown on Figure 9.

The sulfur dioxide rotameter was calibrated by determining analytically the dilution of the sulfur dioxide in a measured stream of nitrogen. The sulfur dioxide was feed into the nitrogen gas stream in the 1-inch diameter glass line to the short wetted wall column. The gas mixture was sampled at a point about six feet downstream from the mixing-point and a series of baffles to promote mixing. The gas sample was taken in an evacuated Gaillard flask of calibrated volume (approximate volume was 300 cm³). The vacuum system was connected directly to the sample point and the Gaillard flask. A mercury manometer was used to measure the pressure in the Gaillard flask before and after admitting the gas sample to the flask.

The flask with the sample was cooled in an ice bath to reduce the pressure sufficiently to allow introduction of 10 cm³ of 0.01 N KIO₃ solution, 0.2 cm³ of 20% KI solution and 2 cm³ of 0.1 N HCl. The KIO₃ oxidized the SO₂ to SO₃ or SO₃-- to SO₄-- and the remainder reacted with hydrogen ion to form I₂ which was titrated with standard thiosulfate solution. The m. equivalents of iodate less the m. equivalents of thiosulfate required for the I₂ gave the m. equivalents of SO₂ in the sample. The ratio of the m. moles of SO₂ to the m. moles of gas in the Gaillard flask gave the mole fraction of SO₂ in

the gas sample. By material balance the sulfur dioxide flow rate was calculated from the metered nitrogen flow rate to calibrate the sulfur dioxide rotameter. When the gas phase was not analyzed during the absorption runs, the gas composition was calculated from the metered flow rates of the nitrogen and sulfur dioxide.

2. Liquid Flow System

The liquid system consisted of a polyethylene feed storage container (approx. 30 gallon capacity) in which the slurries of hydrated lime and calcium carbonate were prepared by mixing the dry powder with distilled water. A centrifugal pump circulated the slurry through a loop of 12-mm glass tubing which extended about four feet above the column with the return leg discharging into the feed storage container. A stirrer in the feed storage container was used in addition to the recirculation to maintain the slurry solids in suspension. A side stream through a small glass line was taken from the upper part of the recirculating loop through a capillary flowmeter and fed directly to the head-piece of the short wetted wall column. The flowmeter was calibrated by direct measurement of the flow.

Liquid effluent from the column which was not needed for sampling for analysis was discharged to the sewer.

3. Liquid Sampling and Analysis

In runs in which a slurry was used as absorbent samples of the effluent liquid were taken from a sampling point immediately below the wetted wall column in flasks purge with N_2 . Operating difficulties in handling the slurry absorbent often interfered with steady operation and to check these conditions duplicate samples were taken ten to twenty minutes after the first set of samples.

In the runs using water as absorbent, the effluent liquid sample stream flowed continuously through a twenty-five ml pipette. After steady state

had been established the pipette was removed from the line, drained to the mark and the measured sample volume introduced under the surface of a known amount of KIO_3 solution.

The effluent liquid was analyzed for calcium hydroxide, carbonate and sulfite. To determine the hydroxide and sum of the carbonate and sulfite concentrations, a 25 ml sample of the slurry was titrated with 0.2 N HCl solution to the phenolphthalein (PH) and methylorange (MO) end points.

The hydroxide concentration in g.mole/liter is given by:

$$\text{Ca(OH)}_2 = \frac{\text{m. eq. HCl (to PH)} - \text{m. eq. (PH to MO)}}{2 \text{ (ml sample)}}$$

The carbonate plus sulfite concentration in g.mole/liter is given:

$$\text{CaCO}_3 + \text{CaSO}_3 = \frac{\text{m. eq. HCl (PH to MO)}}{\text{(ml sample)}}$$

where PH refers to the phenolphthalein endpoint and MO refers to the methylorange endpoint. To determine the sulfite and dissolved sulfur dioxide concentration, an effluent liquid sample (25 ml) was added to a titration flask containing five or ten ml of 0.01 N KIO_3 to which had been added 0.2 to 0.4 ml of 20% KI and two to four ml of 1.0 N HCl. The HCl added in excess dissolved the insolubles in the slurry and released I_2 from the excess KIO_3 not required to oxidize SO_2 and SO_3^{--} . The I_2 was titrated with standardized sodium thiosulfate solution to the starch endpoint.

The oxidizable SO_2 and SO_3^{--} in m. moles/liter is given by:

$$(\text{SO}_2 + \text{SO}_3^{--}) = \frac{(\text{m. eq. KIO}_3 - \text{m. eq. thiosulfate}) 10^3}{2 \text{ (ml sample)}}$$

APPENDIX BSAMPLE CALCULATIONS

Sample calculations are given for the data recorded for tabulated

Run No. 1, Appendix C except as noted otherwise.

Nitrogen Flowrate

Rotameter reading 70.5
 Gas temperature 14.1 °C (287.2 °K)
 Gas pressure (abs) 770 mm Hg
 From Figure 9, $Q_{(STD)} = 2.37$ cu.ft./min.
 $Q_N = (0.638) (2.37) \sqrt{(770/287.2)}$
 $= 2.48$ SCFM

Sulfur dioxide Flowrate

Rotameter reading 4.0
 Gas temperature 24.5 °C (297.6 °K)
 Gas pressure (abs) 759.1 mm Hg
 From Figure 10, $Q_{(STD)} = 0.78 \times 10^{-3}$ cu.ft./min.
 $Q_{SO_2} = (0.626) (0.78 \times 10^{-3}) \sqrt{(759.1/297.6)}$
 $= 0.78 \times 10^{-3}$ SCFM

Gas Analysis (inlet)

Mole fr. $SO_2 = Q_{SO_2} / (Q_N + Q_{SO_2})$
 $= 0.78 \times 10^{-3} / 2.48$
 $= 0.315 \times 10^{-3}$

Liquid Flowrate

Flowmeter reading 201 mm H₂O
 Liquid temperature 23.2 °C
 From Figure 11, Flowrate = 325 cm³/min.
 Diameter of column = 3.18 cm
 Flowrate = $\frac{325}{\pi (3.18)}$ = 32.5 cm³/min-cm

FIGURE 9

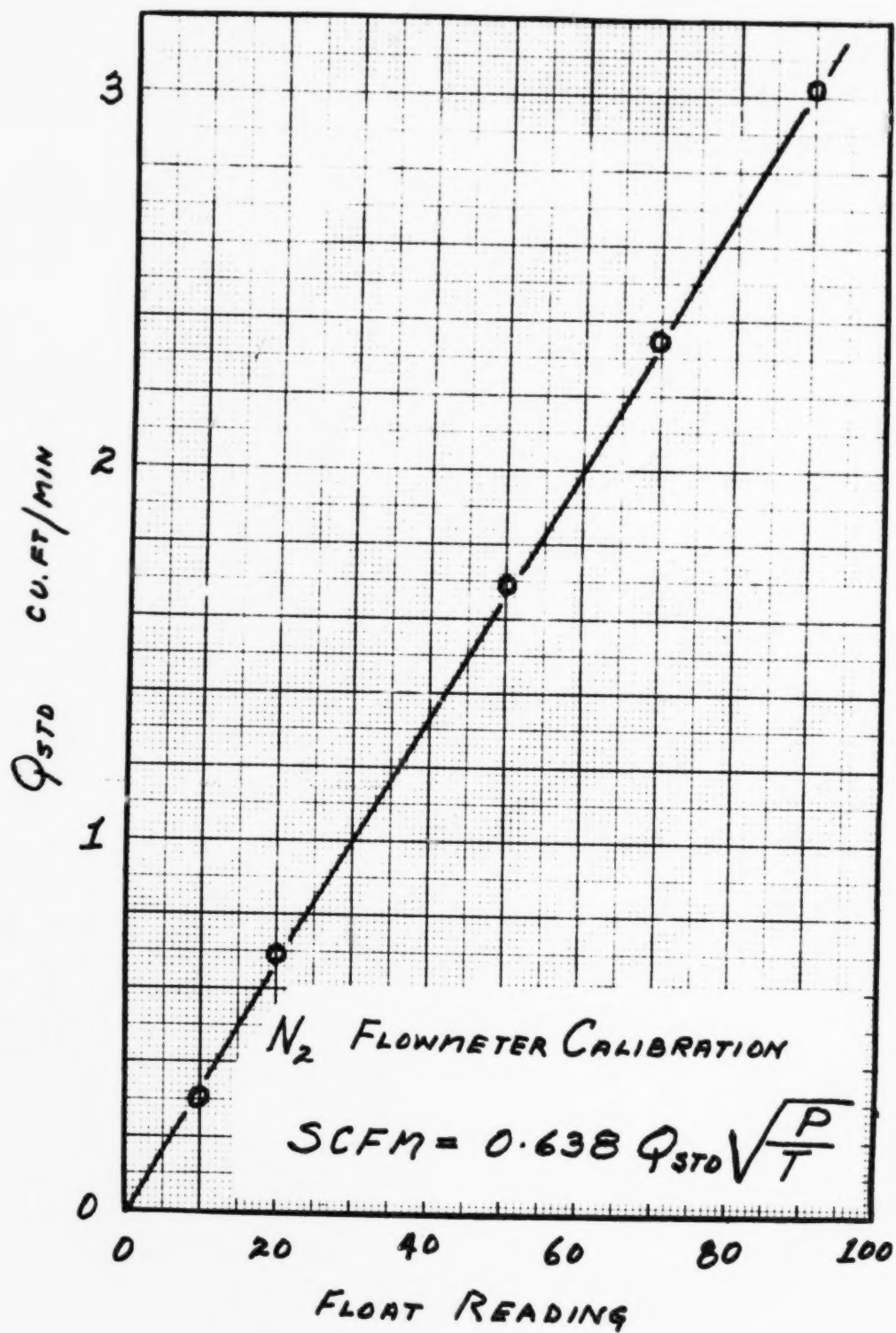


FIGURE 10

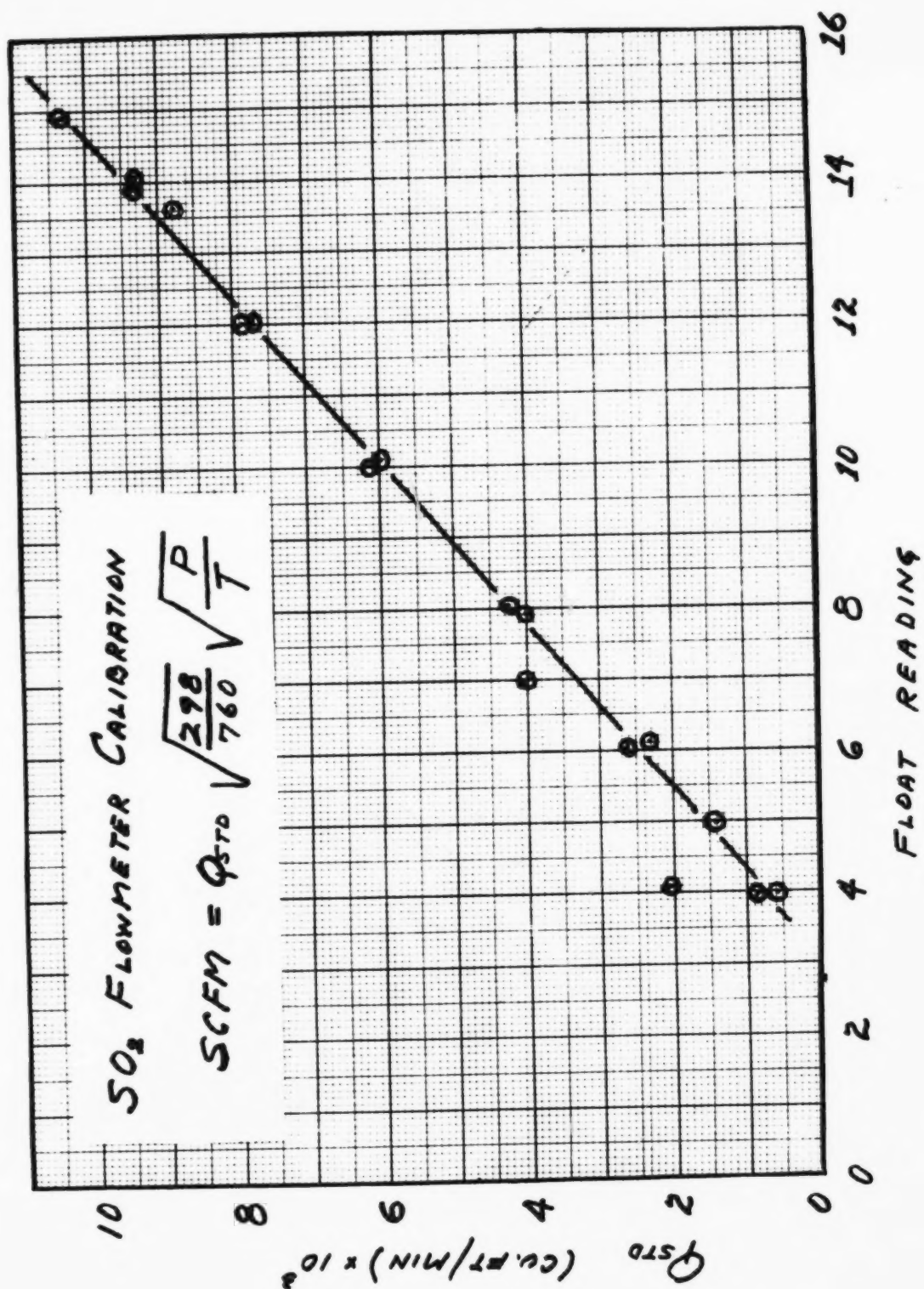
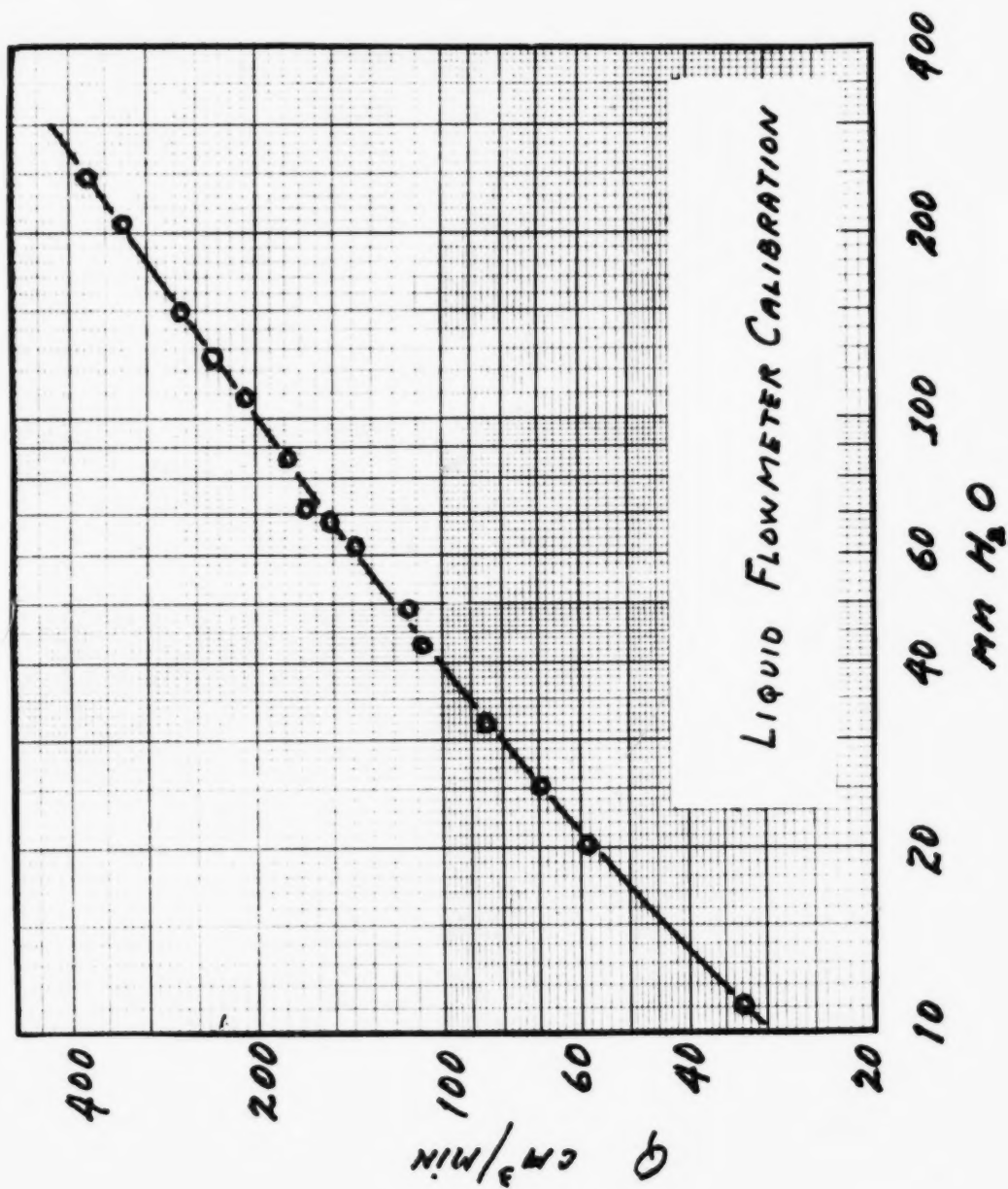


FIGURE 11



Liquid analysis (outlet)

Sample (A) volume 25.0 cm³

Titration with 0.2 N HCl solution

to phenolphthalein endpoint 6.54 m.eq.

to methyl orange endpoint 0.175 m.eq.

total 6.715 m.eq.

$$\text{Ca(OH)}_2 \text{ conc} = \frac{(6.54 - 0.175)}{(2)(25.0)}$$

$$= 0.1273 \text{ g.mole/liter}$$

$$\text{CaCO}_3 + \text{CaSO}_3 \text{ conc} = 0.175/25.0$$

$$= 0.0070 \text{ g.mole/liter}$$

Sample (B) volume 25.0 cm³

KIO₃ solution added 0.1987 m.eq.

Titration with Na₂S₂O₃ solution 0.1882 m.eq.

KIO₃ solution used for SO₂ oxidation

$$= 0.1987 - 0.1882$$

$$= 0.0105 \text{ m.eq.}$$

$$\text{CaSO}_3 \text{ conc} = \frac{0.0105}{(2)(25)} \times 10^3$$

$$= 0.210 \text{ m.mole/liter}$$

$$\text{CaCO}_3 \text{ conc} = 0.00679 \text{ g.mole/liter}$$

Rate of Absorption of SO₂

$$N_A = \frac{(\text{Liquid flowrate})(\text{Outlet CaSO}_3 \text{ conc})}{(\text{Surface area})}$$

$$= \frac{(32.5)(0.210)}{(60)(4.5)(1000)}$$

$$= 25.3 \times 10^{-6} \text{ m.mole SO}_2/\text{sec-cm}^2$$

Overall Gas Phase Coefficients

$$K_G = \frac{N_A}{(P - p^*) 10^3} \quad \text{g.mole/sec-cm}^2\text{-atm}$$

$$K_Y = \frac{N_A}{(Y - y^*) 10^3} \quad \text{g.mole/sec-cm}^2$$

$$(K_G)_G = \frac{N_A}{\rho_G (Y - y^*) 10^3} \quad \text{cm/sec}$$

$$\text{Note that: } K_G = K_Y RT = K_Y / \rho_G$$

$$\rho_G = P/RT$$

$$= \frac{(760.1/760)}{(82.1)(298.7)}$$

$$= 40.7 \times 10^{-6} \text{ g.mole/cm}^3$$

$$(K_G)_G = \frac{(25.3 \times 10^{-6})}{(40.7 \times 10^{-6})(0.250 \times 10^{-3}) 10^3}$$

$$= 2.49 \text{ cm/sec}$$

Gas Phase Resistance

$$\text{Eq No.} \quad N_{Re} = \frac{4Q\mu}{\pi d\mu}$$

$$N_{Re} = (\text{SCFM}) \cdot \frac{(30.5)^3}{(60)} \cdot \frac{(1.0)(28)}{(82.1)(298.1)}$$

$$= (0.541) (\text{SCFM})$$

$$N_{Re} = \frac{(1)(0.541)(2.49)}{(1)(0.18)(0.013 \times 10^{-2})} = 2980$$

Gas phase mass transfer studies in short wetted wall column (9) indicate that:

$$\frac{N_{Sh}}{(N_{Sc})^{1/3}} = 18.5 \text{ at } N_{Re} = 2980$$

The N_{Sc} for SO_2 in N_2 was calculated from data given by Sherwood and Reid, "Properties of Gases and Liquid" McGraw-Hill Book Co., Inc.

$$\text{Diffusivity, } DP = 0.122 \text{ cm}^2\text{-atm/sec at } 273 \text{ }^\circ\text{K}$$

$$\text{At } 298 \text{ }^\circ\text{K and } 1 \text{ atm, } D = 0.139 \text{ cm}^2\text{/sec}$$

$$\text{Gas density, } \rho = 0.00114 \text{ g./cm}^3$$

$$\text{Gas viscosity, } \mu = 0.018 \times 10^{-2} \text{ g./sec-cm}$$

$$\therefore N_{Sc} = 1.136$$

$$\text{and } N_{Sh} = \frac{k_c d}{D} = 18.5(1.136)^{1/3} = 19.3$$

$$(k_c)_G = \frac{(19.3)(0.139)}{(3.18)} = 0.84 \text{ cm/sec}$$

$$\text{Gas phase resistance} = \frac{1}{(k_c)_G} = 1.190 \text{ at } N_{Re} = 2980$$

In this range of N_{Re} , $(k_c)_G$ is approximately proportional to the N_{Re} .

Liquid Phase Coefficients

By definition the liquid phase coefficient for physical absorption is defined by:

$$N_A = k_L^* (C_i - C)$$

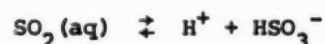
where C is the concentration of the absorbed specie at the interface and in the bulk liquid. When a chemical reaction occurs in the liquid phase involving the absorbed specie, the rate of absorption is also governed by the unreacted specie driving force. The enhancement of the rate due to the

reaction is allowed for by a factor ϕ which depends on the relative rates of reaction and diffusion and which does not depend directly on the fluid dynamics of the process. The rate equation is:

$$N_A = \phi k_L^* (C_1 - C)$$

where C_1 , C refer to the unreacted absorbed specie.

The factor, ϕ , must be defined for the various kinetic schemes encountered. The hydrolysis of SO_2 in water can be written as:



where $\text{SO}_2(\text{aq})$ refers to unhydrolysed molecular SO_2 in solution in water. This reaction is reversible and is believed to be very rapid (1) so that during a diffusion process, equilibrium is maintained between reactants and products.

If C_A is the molecular SO_2 concentration and C_E is the bisulfite ion concentration, the liquid phase equilibrium for SO_2 absorbed into water is given by:

$$K_1 = \frac{(C_E)^2}{C_A}$$

Theoretical analysis assuming film theory for simplicity gives the enhancement factor, ϕ , in terms of the equilibrium concentrations:

$$\begin{aligned} \phi &= 1 + \frac{D_E (C_{Ei} - C_E)}{D_A (C_{Ai} - C_A)} \\ &= 1 + \frac{D_E (\sqrt{K_1} C_{Ai} - \sqrt{K_1} C_A)}{D_A (C_{Ai} - C)} \end{aligned}$$

and the rate of absorption is given by:

$$N_A = \phi k_L^* (C_{Ai} - C_A)$$

If $D_E = D_A$, substituting the expression for ϕ in the rate equation gives:

$$N_A = k_L^* \left[(C_{Ai} + \sqrt{K_1 C_{Ai}}) - (C_A + \sqrt{K_1 C_A}) \right]$$

$$= k_L^* (C_{Ti} - C_T)$$

where C_{Ti} and C_T refer to the total SO_2 in solution (i.e., $SO_2(aq)$ plus HSO_3^-). Furthermore if the concentration of total SO_2 in the bulk is zero, the enhancement factor, ϕ , reduces to

$$\phi = \left(1 + \sqrt{\frac{K_1}{C_{Ai}}} \right)$$

Thus ϕ becomes very large at low partial pressures of SO_2 since $C_{Ai} = H p_i$. This of course shifts the controlling resistance to the gas phase.

Estimation of the value of the enhancement factor, ϕ , for the absorption of SO_2 into calcium hydroxide and calcium carbonate solutions and slurries is complicated by the fact that the H^+ ion concentration is not coupled directly with the bisulfite ion concentration. Consequently, calculation of the ϕ factor is dependent on specification of the H^+ or OH^- ion concentration. These cases have not yet been worked out, and to analyse the experimental data for absorption into calcium hydroxide slurries it will be assumed that the molecular SO_2 concentration at the interface was in equilibrium with the SO_2 concentration in the gas phase at the interface. On this basis the product, ϕk_L^* , can be calculated from the data. ϕ can then be estimated using correlations for physical absorption such as Mayr's equation (4) for k_L^* .

The equilibrium relation connecting gas phase concentration and molecular SO_2 in the liquid is Henry's law:

$$C_{Ai} = H p_i$$

Combining this with the liquid phase rate equation:

$$N_A = \phi k_L^* (C_{Ai} - C_A)$$

we have

$$N_A = \phi k_L^* HP (y_i - y^*)$$

Applying additivity of resistances, we get:

$$\frac{1}{(K_c)_G \rho_G} = \frac{1}{(k_c)_G \rho_G} + \frac{1}{\phi k_L^* HP}$$

$$\text{or } \frac{1}{\phi k_L^*} = \frac{HP}{\rho_G} \left[\frac{1}{(K_c)_G} - \frac{1}{(k_c)_G} \right]$$

Data for Run 3:

$$(k_c)_G = 0.832 \text{ cm/sec}$$

$$(K_c)_G = 0.772 \text{ cm/sec}$$

$$P = 1 \text{ atm}$$

$$\rho_G = 40.7 \times 10^{-6} \text{ g.mole/cm}^3$$

$$T = 26.4^\circ \text{C} (299.5^\circ \text{K})$$

Henry's law constant (see analysis and discussion of equilibrium data p. 6)

$$\ln H = \frac{3175.2}{299.5} - 10.4523 \text{ g.mole/liter-atm}$$

$$H = 1.162 \times 10^{-3} \text{ g.mole/cm}^3\text{-atm}$$

$$\frac{1}{\phi k_L^*} = \frac{(1.162 \times 10^{-3})(1.0)}{(40.7 \times 10^{-6})} \left[\frac{1}{0.772} - \frac{1}{0.832} \right]$$

$$\phi k_L^* = 0.334 \text{ cm/sec}$$

The physical absorption correlating equation due to Mayr is:

$$k_L^* \sqrt{\frac{Z}{D_A}} = 1.759 (\Gamma/\xi)^{0.354}$$

Data for Run 3:

$$z = 4.5 \text{ cm}$$

$$D_A = 1.753 \times 10^{-5} \text{ cm/sec at } 25^\circ \text{C}$$

$$\Gamma = 32.5 \text{ g./min-cm}$$

$$\xi = \mu_T/\mu_{25} \approx 1.0$$

$$\begin{aligned} k_L^* \sqrt{\frac{z}{D_A}} &= 1.759 (32.5)^{0.354} \\ &= 6.03 \text{ (cm/sec)}^{1/2} \end{aligned}$$

$$\sqrt{\frac{z}{D_A}} = 0.505 \times 10^3$$

$$k_L^* = 0.0119 \text{ cm/sec}$$

Then

$$\phi = \frac{(\phi k_L^*)}{k_L^*} = \frac{0.334}{0.0119} = 28.1$$

Enhancement factor for absorption into water

(Data for Run 33)

$$(k_c)_G = 0.84 \text{ cm/sec}$$

$$(K_c)_G = 0.504 \text{ cm/sec}$$

$$P = 1.0 \text{ atm}$$

$$\rho_G = 40.5 \times 10^{-6} \text{ g.mole/cm}^3$$

$$T = 23.4^\circ \text{C} (296.5^\circ \text{K})$$

$$\Gamma = 25.0 \text{ g./min-cm}$$

Henry's law constant

$$\ln H = \frac{3175.2}{296.5} - 10.4523$$

$$H = 1.302 \text{ g.mole/liter-atm}$$

$$= 1.302 \times 10^{-3} \text{ g.mole/cm}^3\text{-atm}$$

$$\frac{1}{\phi k_L^*} = \frac{(1.302 \times 10^{-3})(1.0)}{40.5 \times 10^{-6}} \left[\frac{1}{0.504} - \frac{1}{0.84} \right]$$

$$\phi k_L^* = 0.0392 \text{ cm/sec}$$

$$\sqrt{\frac{z}{D_A}} = 0.532 \times 10^3 (\text{sec/cm})^{1/2}$$

$$k_L^* \sqrt{\frac{z}{D_A}} = 1.759(25.0)^{0.354} = 5.48 (\text{cm/sec})^{1/2}$$

$$k_L^* = 0.0103 \text{ cm/sec}$$

$$\phi = \frac{0.0392}{0.0103} = 3.81$$

Theoretical ϕ

$$\phi = 1 + \sqrt{\frac{K}{C_{A_i}}}$$

$$C_{A_i} = H y_i$$

$$H = 1.302 \times 10^{-3} \text{ g.mole/cm}^3\text{-atm}$$

$$y = 3.16 \times 10^{-3}$$

$$K = 0.019 \text{ g.mole/liter}$$

Applying additivity,

$$y_i = y \left(1 - \frac{(K_c)_G}{(k_c)_G} \right)$$

$$y_i = (3.16 \times 10^{-3}) \left(1 - \frac{0.504}{0.84} \right) = (1.53 \times 10^{-3})$$

$$\begin{aligned} C_{A_i} &= (1.302 \times 10^{-3})(1.0)(1.53 \times 10^{-3}) \\ &= 2.00 \times 10^{-6} \text{ g.mole/cm}^3 \end{aligned}$$

$$\phi = 1 + \sqrt{\frac{0.019 \times 10^{-3}}{2.00 \times 10^{-6}}} = 4.05$$

APPENDIX CSUMMARIZED DATA

TABLE I
Absorption of SO₂ into Lime Slurries

Run	N ₂ Flowrate SCFM	SO ₂ Flowrate SCFM x 10 ³	Gas Flow N ₂	Gas Analysis mole fr. SO ₂ x 10 ³	Total Pressure mmHg	Liquid Temperature °C	Liquid Flowrate cm ³ /min-cm	OUTLET LIQUID ANALYSIS	Abs. Rate x 10 ⁶	(Kc) g/sec	ϕ_{KL}^*	ϕ
1	2.48	0.78	2980	0.315	759.1	25.6	32.5	Total SO ₂ H. mole/L CaCO ₃ g. mole/L Ca(OH) ₂ g. mole/L	25.3	1.97	-	-
2	2.48	0.78	2980	0.315	759.1	26.3	18.5	0.210 0.0068 0.1273	33.3	2.60	-	-
3	2.43	9.02	2950	3.71	759.1	26.4	32.5	0.486 0.0054 0.1263	118.9	0.787	0.661	5.5
4	2.49	8.82	3030	3.54	756.8	25.5	24.0	0.988 0.0346 0.0716	118.8	0.825	1.054	79.8
5	2.49	8.69	3030	3.48	756.8	26.9	11.0	1.337 0.0383 0.0772	116.3	0.821	0.986	117.4
6	2.48	9.02	3020	3.63	756.8	26.4	35.0	2.854 0.0399 0.0644	94.6	0.637	0.115	9.2
7	2.43	9.30	2960	3.83	758.8	32.3	21.5	0.730 0.0385 0.1924	110.7	0.705	0.169	15.1
8	2.45	8.82	2980	3.60	758.8	31.4	7.65	1.390 0.0354 0.1944	106.2	0.719	0.265	34.4
9	3.37	8.92	4080	2.64	765.2	27.9	22.0	3.748 0.0323 0.1664	124.2	1.139	0.007	0.7
10	2.48	9.02	3010	3.64	765.2	29.0	31.5	1.524 0.0191 0.0984	117.4	0.781	0.485	38.8
11	2.42	9.02	2940	3.73	765.2	28.7	8.35	1.006 0.0074 0.0510	84.8	0.550	0.080	9.9
12	2.50	8.82	3040	3.51	765.2	28.5	21.7	2.742 0.0071 0.0416	104.0	0.717	0.213	19.7
13	2.43	2.58	2930	1.06	760.0	28.4	33.0	0.0079 0.0495	36.4	0.831	-	-
14	2.43	2.49	2930	1.025	760.0	28.3	22.8	0.0081 0.1222	40.0	0.945	-	-
15	2.44	2.40	2950	0.982	760.0	28.4	10.8	0.0071 0.1194	35.6	0.878	-	-

TABLE II
Absorption of SO₂ into Lime Solutions

Run	N ₂ Flowrate SCFM	SO ₂ Flowrate SCFM x 10 ³	Gas Flow N re	Gas Analysis mole fr. SO ₂ x 10 ³	Total Pressure mmHg	Liquid Temperature °C	Liquid Flowrate cm ³ /min-cm	Total SO ₂ m. mole/L	CaCO ₃ g. mole/L	Ca(OH) ₂ g. mole/L	M. mole x 10 ⁶	(Kc) _G cm/sec	φ _{KL}	φ
16	2.40	8.95	2920	3.73	763.9	24.5	33.0	0.828	0.0014	0.0138	101.2	0.666	0.150	12.8
17	2.46	6.01	2980	2.45	763.9	25.0	33.0	0.652	0.0013	0.0139	80.4	0.806	0.870	73.1
18	2.43	8.55	2950	3.52	757.2	25.3	33.0	0.734	0.0013	0.0091	89.7	0.626	0.112	9.4
19	2.39	5.97	2900	2.50	757.2	25.8	32.8	0.524	0.0013	0.0093	64.0	0.629	0.112	10.2
20	2.40	3.33	2900	1.39	753.0	24.8	33.0	0.238	0.0006	0.0090	29.1	0.514	0.059	5.0
21	2.40	0.80	2900	0.333	753.2	25.2	32.8	0.048	0.0005	0.0090	5.8	0.428	0.040	3.4
22	2.43	8.61	2950	3.54	762.0	24.7	26.8	0.734	0.0011	0.0118	72.8	0.505	0.055	5.0
23	2.42	6.87	2940	2.84	763.9	23.4	26.8	0.414	0.0009	0.0114	41.1	0.356	0.026	2.5
24	2.41	5.12	2920	2.12	765.0	24.5	26.8	0.518	0.0011	0.0115	51.4	0.560	0.075	6.9
25	2.43	3.37	2940	1.39	768.8	24.6	26.8	0.352	0.0009	0.0112	34.9	0.617	0.104	9.5
26	2.43	8.58	2950	3.53	762.0	25.4	20.0	1.096	0.0016	0.0055	81.2	0.565	0.078	7.9
27	2.40	6.83	2910	2.85	761.0	26.1	20.0	1.068	0.0017	0.0048	79.1	0.682	0.183	17.9

TABLE III
Absorption of SO₂ into Calcium Carbonate Slurries

Run	N ₂ Flowrate SCFM	SO ₂ Flowrate SCFM x 10 ³	Gas Flow N ₂	Gas Analysis mole fr. SO ₂ x 10 ³	Total Pressure mmHg	Liquid Temperature °C	Liquid Flowrate cm ³ /min-cm	Total SO ₂ m. mole/L	CaCO ₃ g. mole/L	Ca(OH) ₂ g. mole/L	Abs. Rate m. mole sec-cm ² x 10 ⁶	(Kc) _G cm/sec	ϕ_{K_L}	ϕ
28	2.38	8.95	2890	3.76	(760)	26.2	32.5	0.714	0.0070	-	85.9	0.561	0.082	7.6
29	2.43	9.00	2950	3.70	767.2	28.9	22.9	0.340	0.0504	-	28.9	0.192	0.012	1.1
30	2.44	2.71	2950	1.11	767.2	28.7	22.9	0.200	0.0546	-	17.0	0.376	0.034	3.1
31	2.43	0.80	2930	0.33	767.2	28.6	23.0	0.200	0.0490	-	17.0	1.265	-	-

TABLE IV
Absorption of SO₂ into Water

Run	N ₂ Flowrate SCFM	SO ₂ Flowrate SCFM x 10 ³	Gas Flow N ₂	Gas Analysis mole fr. SO ₂ x 10 ³	Total Pressure mmHg	Liquid Temp. °C	Liquid Flowrate gm ³ /min-cm	OUTLET LIQUID ANALYSIS Total SO ₂ m. mole liter	ABS. RATE m. mole sec-cm ² x 10 ⁶	(Kc) g/sec	$\frac{dx}{dt}$	
32	2.41	7.60	2910	3.16	765	23.2	25.0	0.599	55.5	0.425	0.0267	2.59
33	2.41	7.50	2910	3.11	765	23.4	25.0	0.690	63.8	0.504	0.0392	3.81
34	2.39	7.45	2880	3.11	765	23.6	13.0	1.174	56.6	0.440	0.0287	3.43
35	2.39	7.60	2880	3.18	765	23.6	13.0	1.195	57.5	0.438	0.0285	3.41
36	2.39	7.50	2880	3.14	765	24.3	41.2	0.615	93.8	0.718	0.1570	11.89
37	2.41	7.45	2910	3.10	765	24.3	41.0	0.517	78.5	0.610	0.0708	5.40
38	2.35	2.70	2840	1.15	765	25.4	25.6	0.365	34.6	0.725	0.1795	16.03
39	2.39	2.70	2880	1.13	765	25.5	25.6	0.343	32.5	0.693	0.1340	11.96
40	2.44	2.70	2950	1.11		25.5	32.4	0.278	33.4	0.725	0.1795	14.71
41	2.44	2.70	2950	1.11		24.8	32.4	0.286	34.3	0.745	0.2231	18.59
42	2.43	2.70	2930	1.11		24.8	20.2	0.444	33.2	0.720	0.1704	16.87
43	2.43	2.70	2930	1.11		24.8	20.2	0.415	31.1	0.675	0.1166	11.54
44	2.43	2.65	2930	1.09	760	26.2	10.6	0.705	27.7	0.613	0.0772	9.27
45	2.43	2.65	2930	1.09	760	26.1	10.6	0.705	27.7	0.613	0.0772	9.27
46	2.44	8.85	2950	3.63	760	28.5	33.8	0.608	76.4	0.507	0.0472	3.66
47	2.44	8.70	2950	3.56	760	27.6	33.5	0.602	74.5	0.504	0.0461	3.63
48	2.40	8.80	2900	3.66	760	28.2	20.2	0.860	64.1	0.433	0.0330	3.08
49	2.47	8.80	2980	3.56	760	28.0	20.2	0.874	65.7	0.433	0.0330	3.08
50	2.47	9.20	2980	3.73	760	26.3	9.5	1.818	64.2	0.415	0.0285	3.56
51	2.47	9.05	2980	3.66	760	26.1	9.5	1.850	65.3	0.430	0.0300	3.75
52	2.41	0.80	2910	0.331	766	25.0	33.0	0.150	18.3	1.33	-	-
53	2.39	0.70	2880	0.293	766	25.0	33.0	0.153	18.7	1.54	-	-
54	2.41	0.90	2910	0.373	766	25.0	20.2	0.312	23.4	1.51	-	-
55	2.39	0.90	2880	0.376	766	25.0	20.2	0.308	23.1	1.49	-	-
56	2.32	0.95	2800	0.410	766	25.3	10.2	0.570	21.3	1.25	-	-
57	2.39	0.95	2880	0.398	766	25.3	10.2	0.607	22.7	1.38	-	-

APPENDIX D
NOMENCLATURE

C	Concentration in liquid phase, g.mole/cm ³ ; subscript A refers to molecular (unhydrolysed) SO ₂ , B to calcium hydroxide, E to bisulfite ion, i to interfacial concentration.
D	Diffusivity, cm ² /sec; subscript A refers to molecular (unhydrolysed) SO ₂ , B to calcium hydroxide, E to bisulfite ion.
d	Column diameter, cm
G	gas rate, g.mole/sec-cm ²
H	Henry's law constant, g.mole/cm ³ -atm
K	Hydrolysis constant for SO ₂ in water, g.mole/cm ³
(K _c) _G	Overall coefficient based on gas phase concentration units, cm/sec.
(k _c) _G	Gas phase coefficient, cm/sec.
k _L [*]	Liquid phase (physical absorption) coefficient, cm/sec.
L	Liquid rate, cm ³ /sec-cm
N _{Sc}	Schmidt number, $\mu/\rho D$
N _{Sh}	Sherwood number, $k_c d/D$
N _{Re}	Reynolds number, $4\Gamma/\mu$ or $4Q\rho/\pi d\mu$
P	Total pressure, atm
p	Partial pressure, atm; superscript * refers to partial pressure in equilibrium with bulk liquid phase.
Q	Gas flow rate, cm ³ /sec or cu.ft./min.
R	Gas constant, 82.1 cm ³ -atm/g.mole - degree K.

T	Temperature, degree K.
y	mole fraction in gas phase
z	Column length, cm

Greek Symbols

Γ	Liquid rate, g./sec-cm
μ	Viscosity, g/sec-cm
ρ	Gas density, g./cm ³ ; subscript G refers to molal gas density, g.mole/cm ³
ϕ	Enhancement factor (dimensionless)

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